

MODIFIED CLAIMS (Art. 34, PCT)

Sub B1

1. Process for the preparation of ~~an~~ emulsion of blocked (poly)isocyanates, ^{said} this process comprising ~~the step consisting in:~~

a) placing an isocyanate composition containing free isocyanate functions in contact with at least one blocking agent A in the presence of a surfactant B and an aqueous phase, the said isocyanate composition being added gradually to at least some of the aqueous phase and at least some of the blocking agent.

2. Process according to Claim 1, ^{wherein} characterized in that the said composition containing an isocyanate function contains, on average, 1 to 5 isocyanate functions per molecule bearing isocyanate function(s).

3. Process according to ^{Claim 1} ~~Claims 1 and 2~~, ^{wherein} characterized in that the said composition containing an isocyanate function contains, on average, 4/3 to 4 isocyanate functions per molecule bearing isocyanate function(s).

4. Process according to ^{Claim 1} ~~Claims 1 to 3~~, ^{wherein} characterized in that the said blocking agent contains at least one labile hydrogen.

5. Process according to ^{Claim 1} ~~Claims 1 to 4~~, ^{wherein} characterized in that the said blocking agent contains at least one labile hydrogen and in that the pKa of the reactive hydrogens is at least equal to 4, advantageously equal to 5, preferably equal to 6, and in that the said pKa is not more than 14, advantageously not more than 13, preferably not more than 12 and even more preferably not more than 10, with the exclusion of lactams.

6. Process according to ^{Claim 1} ~~Claims 1 to 5~~, ^{wherein} characterized in that the pH of the aqueous phase is maintained at a value of not more than 12, advantageously not more than 11, preferably not more than 10, throughout the reaction.

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7. Process according to ^{Claim 1} ~~Claims 1 to 6~~, ^{wherein} ~~characterized in that~~ the pH of the aqueous phase is maintained at a value at least equal to the value (pKa-2), ~~advantageously at least equal to the value (pKa-4), preferably at least equal to the pKa value~~ of the blocking agent, or of one of the blocking agents, throughout the reaction.

8. Process according to ^{Claim 1} ~~Claims 1 to 7~~, ^{wherein} ~~characterized in that~~ the reaction is carried out at a temperature not greater than the cloud point temperature of the surfactant or of the mixture of surfactants used.

9. Process according to ^{Claim 1} ~~Claims 1 to 8~~, ^{wherein} ~~characterized in that the said composition containing an isocyanate function contains a solvent, including a mixture of solvents.~~

10. Process according to ^{Claim 1} ~~Claims 1 to 9~~, ^{wherein} ~~characterized in that~~ the placing in contact is carried out with stirring using a mixer device under conditions which ensure that 90% by mass, ~~advantageously 95% by mass~~, of the particles are between 0.005 and 50 micrometres in size.

11. Process according to Claim 10, ^{wherein} ~~characterized in that~~ the stirring is carried out using a grinding mixer.

12. Process according to ^{Claim 1} ~~Claims 1 to 11~~, ^{wherein} ~~characterized in that~~ the reaction mixture is subjected to recirculation.

13. Process according to ^{Claim 1} ~~Claims 1 to 12~~, ^{wherein} ~~characterized in that~~ the reaction mixture is subjected to recirculation, during which it is subjected to the action of a grinding mixer.

14. Process according to ^{Claim 1} ~~Claims 1 to 13~~, ^{wherein} ~~characterized in that~~ the said placing in contact is carried out by addition of reagent(s) to at least one aqueous phase and at least some of the blocking agent(s).

Sub B4
cont.

15. Process according to ^{claim 1} ~~Claims 1 to 14~~, ^{wherein} ~~characterized in that the said placing in contact is carried out by addition of reagent(s) to a medium containing at least one aqueous phase, at least some of the surfactant(s) and at least some of the blocking agent(s).~~

16. Process according to ^{claim 1} ~~one of Claims 1 to 15~~, ^{said} ~~this process also containing the steps consisting in:~~

b) ^{comprising} ~~subjecting the mixture obtained in a) to a shear (speed gradient) of greater than 1000 s^{-1} , preferably greater than $20,000\text{ s}^{-1}$ and less than $1,000,000\text{ s}^{-1}$, preferably less than $200,000\text{ s}^{-1}$, and~~

c) repeating step b), optionally after step a) has been repeated, until a stable emulsion is obtained whose particles have a Sauter diameter of greater than $0.1\text{ }\mu\text{m}$, ~~preferably $0.2\text{ }\mu\text{m}$, and less than $5\text{ }\mu\text{m}$, preferably less than $2\text{ }\mu\text{m}$, and a dispersion width of less than $5\text{ }\mu\text{m}$.~~

17. Process according to Claim 16, ^{wherein} ~~characterized in that step c) is continued after the end of the addition of the isocyanate composition.~~

18. Process according to Claim 17, ^{wherein} ~~characterized in that step c) is carried out by recirculating the emulsion obtained after step b).~~

19. Process according to ^{Claim 16} ~~any one of Claims 16 to 18~~, ^{wherein} ~~characterized in that the reaction mixture is subjected to recirculation in a colloidal mill.~~

20. Process according to Claim 19, ^{wherein} ~~characterized in that the aqueous phase, to which the isocyanate composition optionally containing the surfactant and/or a solvent is added, is subjected to a first shear (speed gradient) of less than $20,000\text{ s}^{-1}$, preferably less than $40,000\text{ s}^{-1}$, after placing in contact with the blocking agent and before the high-shear step b).~~

a 21. Process according to ^{Claim 1} ~~any one of Claims 1 to 20,~~
 a ^{which} ~~characterized in that~~ it is carried out at a temperature of less than 50°C,
 a ~~preferably less than 40°C.~~

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 a 22. Process according to ^{Claim 1} ~~any one of Claims 1 to 21,~~
 a ^{wherein} ~~characterized in that~~ the surfactant is added to the isocyanate composition
 a in a proportion of less than 20% by weight, ~~preferably less than 10% by~~
 a ~~weight,~~ relative to the weight of the isocyanate composition to be blocked.

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 a 23. Process according to ^{Claim 1} ~~Claims 1 to 22,~~ ^{wherein} ~~characterized in~~
 a ~~that~~ the said surfactant is a surfactant containing an anionic function.

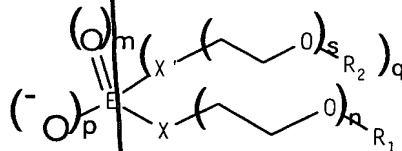
a ^{Sub 1} 24. Process according to ^{Claim 1} ~~Claims 1 to 23,~~ ^{wherein} ~~characterized in~~
 15a ~~that~~ the said surfactant is an anionic surfactant containing at least one
 function chosen from aryl and/or alkyl sulphates or phosphates, aryl or
 alkyl phosphonate, phosphinate and sulphonate.

a 25. Process according to ~~Claims 1 to 24,~~ ^{which} ~~characterized in~~
 20a ~~that~~ it includes a compound containing an anionic function and a
 polyethylene glycol and/or polypropylene glycol chain fragment of at least
 a 1, ~~advantageously at least 5, preferably at least 7,~~ oxyethylene and/or
 oxypropylene units.

25 a ^{Sub B7} 26. Process according to ^{Claim 1} ~~Claims 1 to 25,~~ ^{wherein} ~~characterized in~~
 a ~~that the~~ said compound contains a hydrophilic part formed of the said
 a anionic function, ~~the~~ said polyethylene glycol and/or polypropylene glycol
 chain fragment, and a lipophilic part based on a hydrocarbon-based
 radical.

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 a 27. Process according to ^{Claim 1} ~~Claims 1 to 26,~~ ^{wherein} ~~characterized in~~
 a ~~that the~~ said lipophilic part ^{comprises} ~~is chosen from~~ ^{or} ~~alkyl and~~ aryl groups.

28. Process according to Claims 1 to 27, characterized in that the surfactant is an anionic surfactant, the anionic part corresponding to the following formula:



where q represents zero or 1;

where p represents an integer between 1 and 2 (closed intervals, i.e. including the limits);

where m represents zero or an integer between 1 and 2 (closed intervals, i.e. including the limits);

where X and X', which may be similar or different, represent an arm containing not more than two carbon-based chain members;

where s is zero or an integer chosen between 1 and 30, advantageously between 5 and 25, preferably between 9 and 20 (closed intervals, i.e. including the limits);

where n is zero or an integer chosen between 1 and 30, advantageously between 5 and 25, preferably between 9 and 20 (closed intervals, i.e. including the limits);

where E is an element chosen from carbon and the metalloid elements of atomic rank at least equal to that of phosphorus and belonging to column VB or to the chalcogens of atomic rank at least equal to that of sulphur;

where R₁ and R₂, which may be similar or different, represent a hydrocarbon-based radical advantageously chosen from optionally substituted aryls and alkyls.

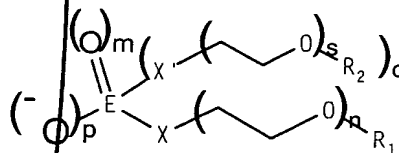
29. Use of ionic surfactant for an isocyanate blocking in emulsion, characterized in that the said surfactant contains a compound containing an anionic function and advantageously a polyethylene glycol and/or polypropylene glycol chain fragment of at least one, preferably of at least 5, oxyethylene and/or oxypropylene units.

30. Use according to Claim 29, characterized in that it contains a compound containing an anionic function and a polyethylene glycol and/or polypropylene glycol chain fragment of at least 5, advantageously of at least 7, oxyethylene units.

Sub A)
31. Use according to Claims 29 and 30, characterized in that the said compound contains a hydrophilic part formed of the said anionic function, the said optional polyethylene glycol chain fragment, and a lipophilic part based on a hydrocarbon-based radical.

32. Use according to Claims 29 to 31, characterized in that the said lipophilic part is chosen from alkyl and aryl groups.

33. Use according to Claims 29 to 32, characterized in that the anionic part of the surface active compound corresponds to formula I below :



where q represents zero or 1;

where p represents an integer between 1 and 2 (closed intervals, i.e. including the limits);

where m represents zero or an integer between 1 and 2 (closed intervals, i.e. including the limits);

where X and X', which may be similar or different, represent an arm containing not more than two carbon-based chain members;

where s is zero or an integer chosen between 1 and 30, advantageously between 5 and 25, preferably between 9 and 20 (closed intervals, i.e. including the limits);

where n is zero or an integer chosen between 1 and 30, advantageously between 5 and 25, preferably between 9 and 20 (closed intervals, i.e. including the limits);

where E is an element chosen from carbon and the metalloid elements of atomic rank at least equal to that of phosphorus and belonging to column VB or to the chalcogens of atomic rank at least equal to that of sulphur;

where R_1 and R_2 , which may be similar or different, represent a hydrocarbon-based radical advantageously chosen from optionally substituted aryls and alkyls.

34. Use according to Claims 29 to 31, characterized in that the counter-cation of the surfactant is an amine, advantageously a tertiary amine.

35. Use according to Claims 29 to 34, characterized in that the said composition containing an isocyanate function contains, on average, 1 to 5 isocyanate functions per molecule bearing isocyanate function(s).

36. Use according to Claims 29 to 35, characterized in that the said composition containing an isocyanate function contains, on average, $4/3$ to 4 isocyanate functions per molecule bearing isocyanate function(s).

37. Use according to Claims 29 to 36, characterized in that the said blocking agent contains at least one labile hydrogen.

38. Use according to Claims 29 to 37, characterized in that the said blocking agent contains at least one labile hydrogen and in that the pK_a of the reactive hydrogens is at least equal to 2, advantageously equal to 3, preferably equal to 5, and in that the said pK_a is not more than 11, advantageously not more than 10, preferably not more than 9.

5 39. Use according to Claims 29 to 38, characterized in that the pH of the aqueous phase is maintained at a value of not more than 12, advantageously not more than 11, preferably not more than 10, throughout the reaction.

10 40. Use according to Claims 29 to 39, characterized in that the pH of the aqueous phase is maintained at a value at least equal to the value (pKa-2), advantageously at least equal to the value (pKa-1), preferably at least equal to the pKa value of the blocking agent, or of one of the blocking agents, throughout the reaction.

15 41. Use according to Claims 29 to 40, characterized in that the mass ratio between the surfactant and the isocyanates is less than 20% and greater than 2%, advantageously between 4 and 10%.

20 *Sub B10* 42. Plant for carrying out the process according to *Claim 16* ~~any one~~ ^{which} ~~of Claims 16 to 41, characterized in that~~ it comprises at least:

~~- a shear means, preferably a mill, advantageously a colloidal mill which can generate a shear rate (speed gradient) of greater than 1000 s⁻¹, preferably greater than 20,000 s⁻¹, and less than 1,000,000 s⁻¹, preferably less than 200,000 s⁻¹; and~~

~~- means for injecting an isocyanate composition into an aqueous phase and optionally one or more of the following means:~~

~~- means for recirculating the aqueous phase in the form of a masked polyisocyanate emulsion;~~

~~- means for regulating the injection flow rate of the isocyanate composition into the aqueous phase;~~

~~- means for homogenizing the emulsion;~~

~~- means for cooling the system; and~~

~~- means for removing the aqueous blocked polyisocyanate emulsion.~~

43. Plant according to Claim 42, ^{wherein} characterized in that the shear means is a colloidal mill.

5 *Sub B11* 44. Plant according to Claim 42 ~~or 43~~, ^{wherein} characterized in that the means for injecting the polyisocyanate composition ^{comprises} comprise:

- a vat for premixing the polyisocyanate with all or some of the surfactant and/or the solvent; and
- an inlet pipe for the polyisocyanate composition in contact with the blocking agent.

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45. Plant according to ^{Claim 42} ~~any one of Claims 42 to 44~~, ^{wherein} characterized in that the recirculation means comprise a recirculation loop.

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46. Composition containing a blocked polyisocyanate emulsion, ^{which} characterized in that it contains a surfactant comprising an anionic function and a polyethylene glycol and/or polypropylene glycol chain fragment of at least 1, ~~preferably at least 5 oxyethylene and/or oxypropylene units~~, said surfactant being present in free form and optionally also bound to the polyisocyanate, with the proviso that when the mean diameter of the particles of the emulsion is less than 5 μm , said surfactant does not contain sulfate groups.

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47. Composition according to claim 46, comprising an emulsion of blocked polyisocyanate(s) ^{which} characterized in that it contains not more than 50 % by weight of water with respect to the weight of the emulsion.

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48. Composition according to claim 46 ~~or claim 47~~, ^{wherein} characterized in that the amount of blocked polyisocyanate(s) in the emulsion represents at least 55 % by weight with respect to the total weight of the emulsion.

Claim 46

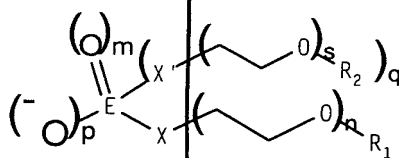
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Claim 47

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Sub A2

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where n is zero or an integer selected between 1 and 30, advantageously between 5 and 25, preferably between 9 and 20 (closed intervals, i.e. including the limits);

where E is an element selected from carbon and the metalloid elements of atomic rank at least equal to that of phosphorus and belonging to column VB or to the chalcogens of atomic rank at least equal to that of sulphur;

5 where R₁ and R₂, which may be similar or different, represent a hydrocarbon-based radical advantageously selected from optionally substituted aryls and alkyls.

10 53. Composition according to any one of claims 46 to 52, characterized in that it has a viscosity of less than 5500 mPa.s at at least 68% solids, at 25°C, and, advantageously, a viscosity of less than 1000 mPa.s at at least 60% solids, at 25°C.

15 54. Composition according to any one of Claims 46 and 53, characterized in that it also contains a release catalyst, which is advantageously a latent catalyst.

20 *Sub B15* 55. Composition according to *claim 46* ~~any one of Claims 46 to 54,~~ *which* characterized in that it contains at least one polyol. *^*

a 20 *a* 56. Composition according to *claim 46* ~~any one of Claims 46 to 55,~~ *wherein* characterized in that the said polyol is a nanolatex whose d₈₀ is not more than 1 micrometre. *^*

a 25 *a* 57. Composition according to *claim 46* ~~any one of Claims 46 to 56,~~ *which* characterized in that it contains an isocyanate emulsion whose d₈₀ is not more than 10 micrometres. *^*

a 30 *a* 58. Composition according to *claim 55* ~~any one of Claims 55 to 57,~~ *wherein* characterized in that the water content is between 10 and 70% (oil-in-water emulsion). *^*

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59. Composition according to ^{claim 55} ~~Claims 55 to 58~~,
^{wherein} ~~characterized in that~~ the content of isocyanate + emulsifier + alcohol is
 between 30 and 70%.

60. Process for producing coatings, ^{comprising} ~~characterized in that it~~
 contains the following steps:

- application of the composition according to ^{claim 46} ~~one of Claims 40~~
~~to 59~~ in the form of a layer of between 20 μ m and 200 μ m in thickness, and
- heating to a temperature at least equal to 80°C.

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Sub B16

61. Coating, ^{which} ~~characterized in that~~ it can be obtained by
 carrying out the process according to Claim 60.

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C1